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The electronic factor and related redox processes in oxidation catalysis

Jean-Marie Herrmann *

Laboratoire d'Application de la Chimie à l'Environnement (LACE), UMR CNRS 5634,
Université Lyon 1, 43 bd du 11 novembre 1918, Villeurbanne Cedex, France

Dedicated to the late Professor Paul Grange (1943–2003).

Abstract

Catalysis by oxides concern mild selective oxidation as well as total oxidation reactions. Oxides are all semiconductors, either pure, mixed, doped or supported and the redox reactions they catalyse are all connected with their electronic properties. n-Type semiconductors possess anionic vacancies which, when once or twice ionized, are the real oxidative agent of the oxide catalyst. This is illustrated by the Sn–Sb–O system. p-Type oxide semiconductors have positive holes h^+ as charge carriers, associated with an excess of anionic oxygen. They are illustrated by the case study of vanadyl-pyrophosphate $(VO)_2P_2O_7$ able to selectively oxidize butane into maleic anhydride in a single pass. In situ measurements of the electrical conductivity of titania during the catalytic oxidation of CO clearly indicated that the oxidizing agent was O^- species. All what is described in thermal catalysis can be transposed to photocatalysis at room temperature, with the simultaneous formation of photoelectrons and holes. In dry medium (gas or liquid phase), selective mild oxidation occur involving a neutral activated species O^*, illustrated by the direct oxidation of 4-*tert*-butyl-toluene into 4-*tert*-butyl-benzaldehyde.

Keywords: Electron factor; Redox process; Electrical conductivity; Oxygen active species; Photocatalysis; Oxidation catalysis; Mild oxidation

1. Introduction

Oxidation catalysts are mainly oxides and used in a large variety of states, either pure or mixed (binary, ternary...), or doped or deposited. They are exclusively semiconductors, i.e., by definition, their electrical conductivities σ vary exponentially with temperature. Since oxidation catalysis is typically a Redox process, this underlines the fundamental role of the electronic factor (EF) [1]. The technique used is the electrical conductivity measurement, which has been successfully applied to the following studies; (i) identification of structure defects in n-type, p-type pure oxide catalysts in doped, mixed and supported oxides in other chalcogenides (mixed sulphides and perovskites); (ii) in situ determination of the phase transition temperatures of catalysts by temperature programmed electrical conductivity (TPEC); (iii) Identification of oxygen active species and determination of redox processes in reaction mechanisms by in situ, *operando*, *combinando* electrical conductivity measurements during catalysis and (iv) the fundamentals of photocatalysis by in situ electrical photoconductivity measurements:In what follows, a review is presented on the electron factor in oxidation catalysis which concerns the European Project ‘‘Concorde’’.

2. Recall of definitions

2.1. Conductors

A conductor is characterized by its electrical conductivity σ which is proportional (i) to the electrical charge concentration n; (ii) to Coulombic value of these elementary charges q and (iii) to their mobility μ:

$$\sigma = nq\mu$$

Actually, the electrical conductivity of solids extends upon about 50 orders of magnitude, from insulators to superconductors as illustrated by the axis in Scheme 1 taken in ref. [1].

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* Tel.: +33 472 43 29 79; fax: +33 472 44 84 38.
E-mail address: jean-marie.herrmann@univ-lyon1.fr.

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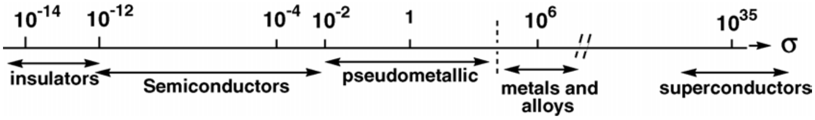


Scheme 1. Logarithmic values of σ for all the different types of conductors (from ref. [1]).

This illustrates that electrical conductivity measurements can be very sensitive, often more than other physical methods.

2.2. Semiconductors

By definition, a semiconductor is a conductor whose electrical conductivity σ is ‘‘activated’’, i.e., varies exponentially with T because of the mass action + Van t’ Hoff’s laws, according to:

$$\sigma = \sigma_o \exp(-E_c/RT).$$

2.3. Classification of semiconductor oxides

All oxides can be classified as intrinsic and extrinsic semiconductor oxides. Intrinsic semiconductors have their electrical conductivity originating from inner ionization induced by elevated temperature. Extrinsic semiconductors oxides can be divided into p-type (by oxidation) and n-type (by reduction). The selection criterion is the sign of the derivative $\partial\sigma/\partial P_{O_2}$.

2.4. p-type semiconductor oxides

$\partial\sigma/\partial P_{O_2} > 0$. They are characterized by an excess of lattice O^{2-} anions, $M^{x+}O^{2-}_{(x/2)+\varepsilon}$. They are much less numerous than n-type ones (NiO, Cu_2O…) but the case of vanadyl pyrophosphate is particularly interesting (see further).

2.5. n-type semiconductor oxides

$\partial\sigma/\partial P_{O_2} < 0$: They are the most abundant oxides (TiO_2, ZnO, SnO_2, CeO_2, ZrO_2, Nb_2O_5,…). Their reactivity is related to their anionic sub-stoichiometry $M^{x+}O^{2-}_{(x/2)-\varepsilon}$ (deficit in lattice O^{2-} anions) accounted for by the existence of anionic vacancies V_O^{2-}.

$$O^{2-}_{(\text{lattice})} \rightleftarrows \tfrac{1}{2}O_2(g) + V^{-}_{O_2}$$

V_O^{2-} corresponds to a neutral entity with respect to the lattice (also called neutral helium center) which can lose its 1st and its 2nd electron by increasing T.

$$V_O^{2-} \rightleftarrows (V_O^{2-})^{+} + e^{-}$$

$(V_O^{2-})^{+}$: singly ionized anion vacancy

$$(V_O^{2-})^{+} \rightleftarrows (V^{-}_{O_2})^{2+} + e^{-}$$

$(V_O^{2-})^{2+}$: doubly ionized anion vacancy

Actually, in oxidation catalysis, the oxidizing species inherent to the n-type SC oxide catalyst cannot be the surface anions O_S^{2-}, already at the minimum -2 oxidation state but essentially singly or doubly ionized anionic vacancies depending on the temperature range.

2.6. Doped semiconductor oxides

By definition from electronics, a doped (oxide) semiconductor is a semiconductor in which one has artificially introduced a ‘‘homeopathic’’ ($\leq$1 at.%) and controlled amount of heterovalent cationic ‘‘impurities’’, whose presence controls the electrical conductivity. The conditions required are (i) several valencies of the host cation M^{n+}; (ii) a difference of valency at least equal to 1 and (iii) a true solid solution with compatible ion sizes [2]. A schematic of n- and p-type doping of titania is given in Fig. 1.

In n-type semiconductor oxide, if the impurity valency is larger than that of the host cation valency, one gets a n-type doping with donor centers D. If the impurity valency is smaller than that of the host cation valency, one gets a p-type doping with acceptor centers A.

3. n-type semiconductors: Case study of Sn–Sb–O system

Electrical conductivity could establish all the features of binary mixed Sn–Sb–O mixed oxides from SnO_2 to Sb_2O_4.

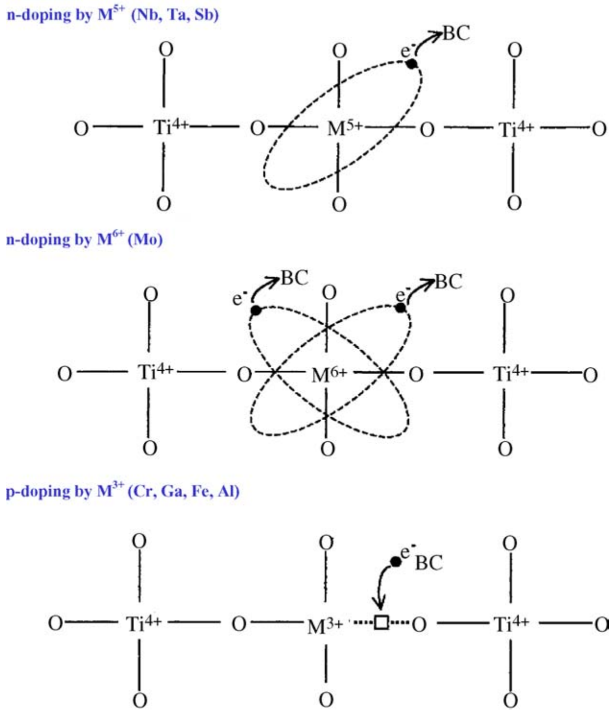


Fig. 1. Schematic of n-and p-type doping of titania.

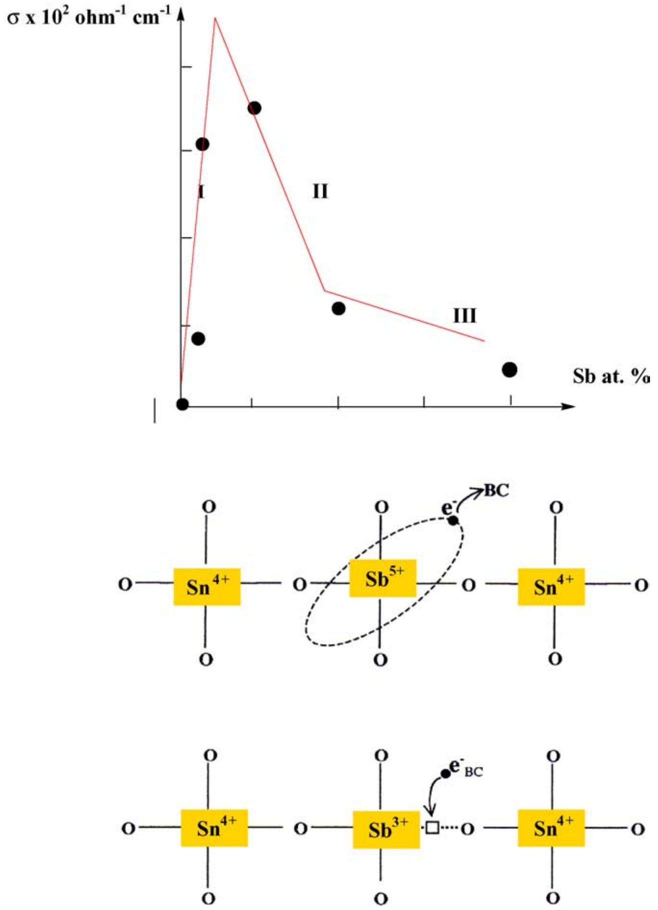


Fig. 2. Conductivity of Sn–Sb–O solid catalysts for Sb $\leq$ 40 at.% (after ref. [1]).

SnO_2 behaves as a pure n-type SC with singly ionized anionic vacancies confirmed by the relationship $\sigma \propto P_{O_2}^{-1/4}$. By contrast, Sb2O4 is an intrinsic semiconductor. By adding Sb to SnO_2, Sb dissolves first exclusively as Sb^{5+} in SnO_2 up to 6.1 at.%, then dissolves as (Sb^{5+} + Sb^{3+}) for 6.1 $\leq$ Sb $\leq$ 20%. At Sb = 20 at.%, the solution of Sb^{5+} and Sb^{3+} becomes saturated and the Sb_2O_4 phase begins to appear with a progressive increase up Sb $\simeq$ 40 at.% (Fig. 2). For Sb $\geq$ 70 at.%, the solid tends to the Sb_2O_4 phase with a n-type doping induced by the dissolution of Sn^{4+} in Sb^{3+} sites of Sb_2O_4. All these domains of Sb valencies were later confirmed by Mössbauer spectroscopy. The electronic conductivity could also explain two other features: (i) the calcination of Sn–Sb–O at 900 °C induced an enrichment in Sb^{5+} of the surface detrimentally to the bulk and (ii) the addition of Fe^{3+} stabilized the solid solution of Sb^{5+} in SnO_2 versus T by an associated p-type doping of iron Fe^{3+} in Sn^{4+} sites.

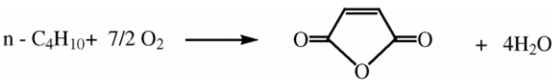
$$: \{(Fe^{3+})_{\text{dissolved}} + [(Sb^{5+})e^{-}]_{\text{dissolved}} \rightleftarrows [(Fe^{3+})e^{-}] + (Sb^{5+}),$$

$$\text{or } A + D \rightleftarrows A^{-} + D^{+}$$

Actually, the most active and selective catalyst in the oxidation of propene in acrolein is the solid solution of Sb in SnO_2 supporting a nano Sb_2O_4 phase.

4. p-type semiconductor oxides: case study of $(VO)_2P_2O_7$

As mentioned above, they are much less numerous than n-type ones but the case of vanadyle pyrophosphate is particularly interesting since $(VO)_2P_2O_7$ is able, in a single pass, to convert n-butane (a side product in oil industry) into maleic anhydride, a valuable cyclic oxygenated molecule.



This selective and complex oxidation has to be directly associated to the excess of anionic oxygen responsible for the p-type semiconductor $(VO)_2P_2O_7$, which is not only able to first oxydehydrogenize *n*-butane but also to insert oxygen atoms into the oxygenated final product.The "respiratory" redox behavior of VPO catalysts is illustrated by Fig. 3 where are presented kinetics curves $\log \sigma = f(t)$ during alternative sequences: Air, butane, O_2, butane, O_2 and eventually the reacting mixture (butane + O_2). There appears that (i) VPO is a p-type semiconductor since $\partial\sigma/\partial P_{O_2} > 0$, (ii) σ oscillates within 3 orders of magnitude and (iii) the solid is in an oxidized state during reaction. The charge carriers are holes h^+ linked to the presence of V^{5+} in VPO. The reaction mechanism is based on the initial oxydehydrogenation of butane in butene

- 1st H abstraction: $C_4H_{10} + h^+ \rightarrow C_4H_9{}^\circ + H^+$
- 2nd H abstraction: $C_4H_9{}^\circ + h^+ \rightarrow C_4H_8 + H^+$

The protons are eliminated as water plus a doubly ionized anionic vacancies which is then filled by gaseous oxygen, thus regenerating the two holes previously consumed.

$$O^{2-} + 2H^{+} \rightarrow H_2O + V_{O^{2-}}^{2+}$$

$$V_{O^{2-}}^{2+} + 1/2O_2(g) \rightarrow O^{2-} + 2h^{+}$$

Fig. 3 clearly illustrates the reversible redox processes which occur similarly in the conductivity cell and in the recirculating solid reactor described by Contractor in ref [3]. VPO behaves actually as a "solid reactant" which is reduced by butane and requires to be reoxidized by oxygen from the air.

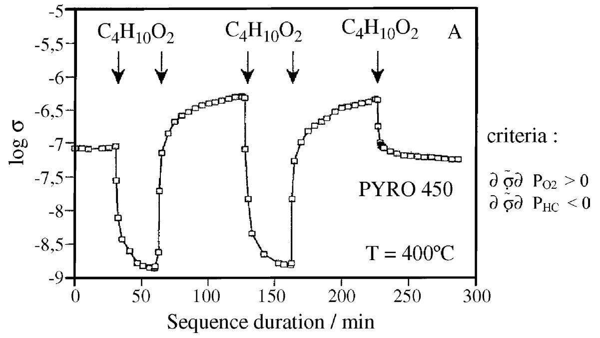


Fig. 3. "Respiratory" redox behaviour of VPO during the oxidation of butane in maleic anhydride.

5. In situ and *operando* electronic conductivity measurements in a "cell reactor" during catalysis

The principle of the experiments is to perform simultaneous kinetics measurements (i) of the reaction rate r and (ii) of the electrical conductivity σ of the catalysts in a differential flow reactor-cell [4]. It is described in Fig. 4.

From the relationship $r = f(\sigma)$ including the kinetics parameters of the reaction (temperature, total and partial pressures), one would expect a clear identification of the active species. CO oxidation on TiO_2 has been selected since it is a univoque reaction with 100% selectivity in CO_2 to facilitate the interpretation of the simultaneously and correlated electrical and catalytic data.

Temperature T was varied under two conditions: (i) under pure N_2 carrier gas, σ varied exponentially with T, with a corresponding activation energy (or enthalpy) of conduction equal to: $E_c = 18.5$ kcal/mol. (ii) under reaction mixture: two simultaneous kinetic data were obtained:

$$r = a'_o \exp(-E_a/RT) \text{ and } \sigma = \sigma'_o \exp(-E'_c/RT)$$

with two simultaneous activation energies: $E_a = 24.5$ kcal/mol and $E'_c = 34.5\,\text{kcal/mol}$.

By maintaining constant one pressure of reactant and varying the other pressure, one could determine the partial orders of O_2 and CO not only for the reaction rate but also for conductivity σ

$$r = k_a P_{O_2}^{0.12} P_{CO}^{0.72} \text{ and } \sigma = k_\sigma P_{O_2}^{-0.51} P_{CO}^{0.33}$$

The additivities of the fractional partial orders when varying the total pressure was found excellent, which demonstrates that the four partial orders determined are all true orders.

Interpretation

How to solve this puzzle? How to correlate all these double kinetic data ? As in most cases in heterogeneous catalysis, let us assume a Langmuir–Hinshelwood mechanism, based on the four following elementary steps:

$$CO_{(g)} + S \rightarrow CO_{(ads)} \tag{1}$$

$$CO_{(ads)} + O^-_{(ads)} \rightarrow CO_{2(ads)} + e^- \tag{2}$$

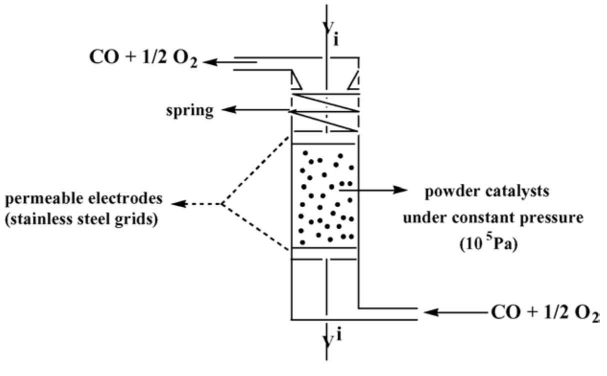


Fig. 4. Principle of the dynamic differential flow cell-reactor.

$$CO_{2(ads)} \rightarrow CO_{2(g)} + S \tag{3}$$

$$O_{2(g)} + 2e^- \rightarrow 2O^-_{(ads)} \tag{4}$$

where S is an adsorption site for CO, e^- is a "quasi-free" conduction electron in the conduction band originating from anionic vacancies detected under pure nitrogen carrier gas and $O^-_{(ads)}$ is proposed as the active oxidizing species able to oxidize CO into CO_2. It can be recalled (see above) that this species cannot be $O^{2-}_{(ads)}$, which is already in the -2 oxidation state. The hypothesis of a Langmuir–Hinshelwood mechanism implies that the rate limiting step is the rate of the reaction occurring in the absorbed phase. Therefore: $r = r_2 = k_2\theta_{CO}\ [O^-_{(ads)}]$. The principle of the stationary state applied to the oxidizing species $O^-_{(ads)}$ implies:

$$d[O^-_{(ads)}]/dt = 2k_4 P_{O_2}[e^-]^2 - k_2\theta_{CO}[O^-_{(ads)}] = 0$$

Thence

$$[e^-] = \frac{(k_2\theta_{CO}[O^-_{(ads)}])^{1/2}}{(2k_4)^{1/2}P_{O_2}^{1/2}} = \frac{r_{1/2}}{(2k_4)^{1/2}P_{O_2}^{1/2}}$$

There results that the reaction rate r and conductivity σ are permanently linked by the relationship:

$$\sigma \propto (r/P_{O_2})^{1/2} \Leftrightarrow r \propto \sigma^2 P_{O_2}$$

If this relationship is true, it should be checked with respect to the combinations between (i) electrical and kinetic partial orders and (ii) activation energies. Since one has: $\sigma \propto (r/P_{O_2})^{1/2}$ with $r = kP_{O_2}^{0.12}P_{CO}^{0.72}$, therefore, the partial electrical orders n and m for oxygen and CO respectively given by $\sigma = k_\sigma P_{O_2}^n P_{CO}^m$ should be equal to: $n = (0.12)/2-0.5 = -0.44$ and $m = (0.72)/2 = 0.36$. The experimental values found (−0.51 and +0.33) are in satisfactory agreement. From the thermal point of view, by combining the two equations $\sigma = f(T)$ (i) under N_2 carrier gas and (ii) under reaction conditions, one gets:

$$\sigma(T) = A[e^-] = \sigma_o \exp(-E_c/RT) \times \frac{r_O^{1/2}\exp(-E_a/2RT)}{(2k_4)_O^{1/2}\exp(-E_4/2RT)}$$

$$\text{Therefore}: E'_c = E_c + E_a/2 - E_4/2$$

Considering the re-oxygenation of the surface is a fast and unactivated reaction (Eq. (4)), the relationship between electrical and kinetic activation energies was found observed within less than 10%. According to the solution of the "double kinetic puzzle" including simultaneously σ, r T, P_{O_2}, P_{CO}, there results that the active oxidizing species on TiO_2 in the 400–480 °C temperature range, is a dissociated, singly charged, oxygen species: $O^-_{(ads)}$. The *operando* results enable one to rule out all other known oxygen species: O_2^-, O and O^{2-}. O_2^-, which is already very improbable because of the temperature range, would have given: $\sigma \propto (r/P_{O_2})$. The neutral species $O_{(ads)}$ must be also ruled out since it would have given: $\sigma \propto (r/P_{O_2})^{1/2}$ which is also not conform to the kinetic equations. Eventually, $O^{2-}_{(ads)}$ and/or O^{2-}_S which are inherently "non-oxidizing" species because of their 2-oxidation state, would have given $\sigma \propto (r^{1/2}/P_{O_2}^{1/4})$, which is not conform to reality. This study clearly enabled one to identify the active oxygen species. A more complex oxidation reaction should be selected in the future to correlate σ to selectivity.

6. Mild and total oxidation in photocatalysis

This recent subdiscipline of catalysis is able to produce, *at room temperature*, either selective mild or total oxidations. The redox reactions are based on photoinduced electronic processes:

$$(TiO_2) + h\nu \rightarrow e^- + h^+ \qquad (h\nu \geq E_G,\ \text{band gap}).$$

Mild oxidations only occur in water-free organics (gas or liquid) media where the hole h^+ is the oxidizing species. For instance, one could selectively oxidize 4-tertio-butyl-toluene in 4-tertio-butylbenzaldehyde. This oxidation which intervenes in fine chemistry is industrially performed by the stoichiometric oxidation of 4-TBT by permanganate according to:

$$5C_4H_9 - C_6H_4 - CH_3 + 4KMnO_4 + 6H_2SO_4$$
$$\rightarrow 4MnSO_4 + 2K_2SO_4 + 11H_2O + 5C_4H_9 - C_6H_4 - CHO$$

This generates a lot of organic and inorganic undesirable by-products. By contrast, the 100% selective reaction, gives no by-products and only uses titania, UV-A photons and oxygen from the air! This is a typical "Environmentally Friendly Green Chemical" process.

$$\text{4-tert-}C_4H_9{-}C_6H_4{-}CH_3 + O_2(\text{air} + TiO_2 + h\nu)$$
$$\rightarrow \text{4-tert-}C_4H_9{-}C_6H_4{-}CHO + H_2O$$

In addition and by contrast, in water or in humid air, holes preferentially react with water and generate OH° radicals: $h^+ + (H_2O) \rightarrow H^+ + OH^{\circ}$ which are known as the second best oxidizing agent after fluorine. Therefore, aqueous photocatalysis is able to destroy any organic chemicals into $CO_2 + H_2O$ [5].

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